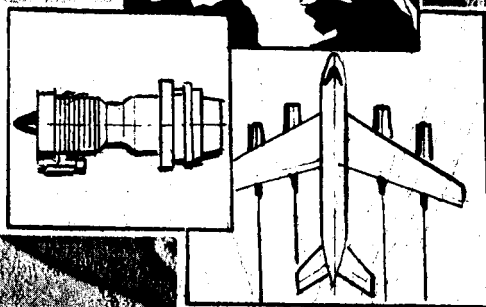


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DM 63-233



104-10088

Code 41

RESEARCH ON ANALYTICAL METHODS FOR OXYGEN IN LIQUID ALKALI METALS

CONTRACT NO.: NASr-12 & CONTROL NO. HS-716

PERIOD COVERED: (Final Report) April 1, 1963 to August 31, 1963

AUTHORS: H. Kirtchik/T. Lajcik

NASA CR 52184

Materials Development Laboratory Operation

Advanced Engine Technology Department

GENERAL  ELECTRIC

CINCINNATI 15, OHIO

September 30, 1963

OTS PRICE

XEROX

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3.60 ph

MICROFILM

\$

1.19 mf.

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(NASA) Contract No. NASr-12 /
Control No. HS-716

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September 30, 1963 33 p & ref

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Materials Development Laboratory Operation

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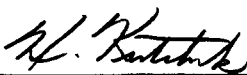
PREPARED FOR: Materials Division, Office of Advanced Research Programs
NASA, Washington, D. C.

TITLE: RESEARCH ON ANALYTICAL METHODS FOR OXYGEN IN LIQUID ALKALI METALS


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INTRODUCTION

In the Quarterly Report #9, April 15, 1963, it was noted that neither fluorine nor anhydrous hydrogen fluoride could be obtained oxygen-free. Also, neither could be purified sufficiently in the laboratory to qualify as reagents for the determination of small amounts of oxygen in another substance such as potassium. "Oxygen-free" fluorine and "anhydrous hydrogen fluoride" continually gave exceedingly high and unmanageable blanks of oxygen in the apparatus system.

To overcome the above shortcomings, the report suggested substitution of bromine trifluoride for fluorine, noted some of the expected reactions, and described the work to be done during the ensuing quarter.

This final report describes the work done with bromine trifluoride, BrF_3 . The additional months of July and August were supported by an amendment to the original NASr-12 contract.

SUMMARY

1. The present study has conclusively established the feasibility of developing a specific method for the analysis of traces of oxygen (5 to 150 ppm) in alkali metals. The method is based on the reaction of purified bromine trifluoride (BrF_3) with the subject metal to liberate molecular oxygen which is then dynamically determined by the Brady method.
2. An apparatus has been designed and constructed to purify and accommodate the BrF_3 in a reaction system and to sweep, with purified helium, the liberated oxygen to a spectrophotometric measuring instrument.
3. When reacted with bromine trifluoride, excellent recoveries of oxygen were obtained on test samples of potassium bromate (KBrO_3) containing between 25 and 150 micrograms of oxygen. Thus, the BrF_3 method is applicable for analytical purposes at concentration levels as low as three orders of magnitude less than previously reported in the literature.
4. The feasibility of applying the present method to potassium has been demonstrated qualitatively by the reaction of BrF_3 with a contaminated potassium sample, which resulted in a large measurable recovery of oxygen. These tests also showed that BrF_3 can be made under specific conditions to react in a controllable manner with potassium metal without observable difficulties.
5. To properly adapt this Bromine Trifluoride Method for the specific analysis of oxygen in such elements as potassium and sodium, improvements in apparatus and instrumentation must be made and statistical data obtained using reliable alkali metal samples.

EXPERIMENTAL PROCEDURE AND RESULTS

Emeleus and Woolf⁽¹⁾ had shown that bromine trifluoride reacted with a number of metallic oxides to quantitatively liberate molecular oxygen. Representing the metal ion by M:



It was quickly shown by Emeleus as well as others^(2,3) that while some oxides gave incomplete recoveries, the criterion for quantitative results was that a volatile or reagent soluble fluoride must form. In addition, certain oxy-salts such as the iodates and bromates gave a complete reaction with the bromine trifluoride. Further, the literature without qualification reports that BrF₃ may be obtained free of oxygen itself.

The common practice was to use oxide samples to liberate as much as 75 milliliters or 0.1 gram of oxygen. Only static systems were used and after equilibration, the oxygen level was obtained by pressure measurements. To determine the oxygen content of a sample, the material was put into a fluocarbon plastic tube at liquid nitrogen temperature and the apparatus evacuated. Then the reaction tube was heated to approximately 75°C. The pressure of the evolved oxygen was measured with a differential mercury manometer.

While the oxides of the alkali metals were not among those studied by others, they should qualify for complete liberation of oxygen because of the high solubility of the corresponding fluorides in bromine trifluoride⁽⁴⁾.

All of the above suggested that the substitution of BrF_3 for F_2 would allow for the determination of oxygen in alkali metals by the fundamental approach suggested in previous reports.

Following the proposed outline in the previous report⁽⁵⁾, the apparatus was constructed as shown in Figure 1. Means for introducing both bromine trifluoride and anhydrous hydrogen fluoride to the Reaction Cell were provided. It was soon found that while BrF_3 and HF were compatible, vapors of hydrogen fluoride escaped condensation in the Monel and Kel-F aft-train cold traps during the sweep of the system with helium. When the Reaction Cell was kept at -30 to -40°C to receive the potassium, the hydrogen fluoride vapor was deemed excessive. The HF was difficult to retain in the whole aft-system prior to the Brady Apparatus. When the gas reached the latter, analytical interference resulted.

The mixture of HF and BrF_3 would initially generate molecular oxygen from any water originally present in the "anhydrous hydrogen fluoride". For equilibration, raising the temperature of the solution to at least $22 - 24^\circ\text{C}$ would be required. Prior to any blank determination of the system, the oxygen so generated would have to be swept out with helium and, hence, result in a high volatilization of the HF.

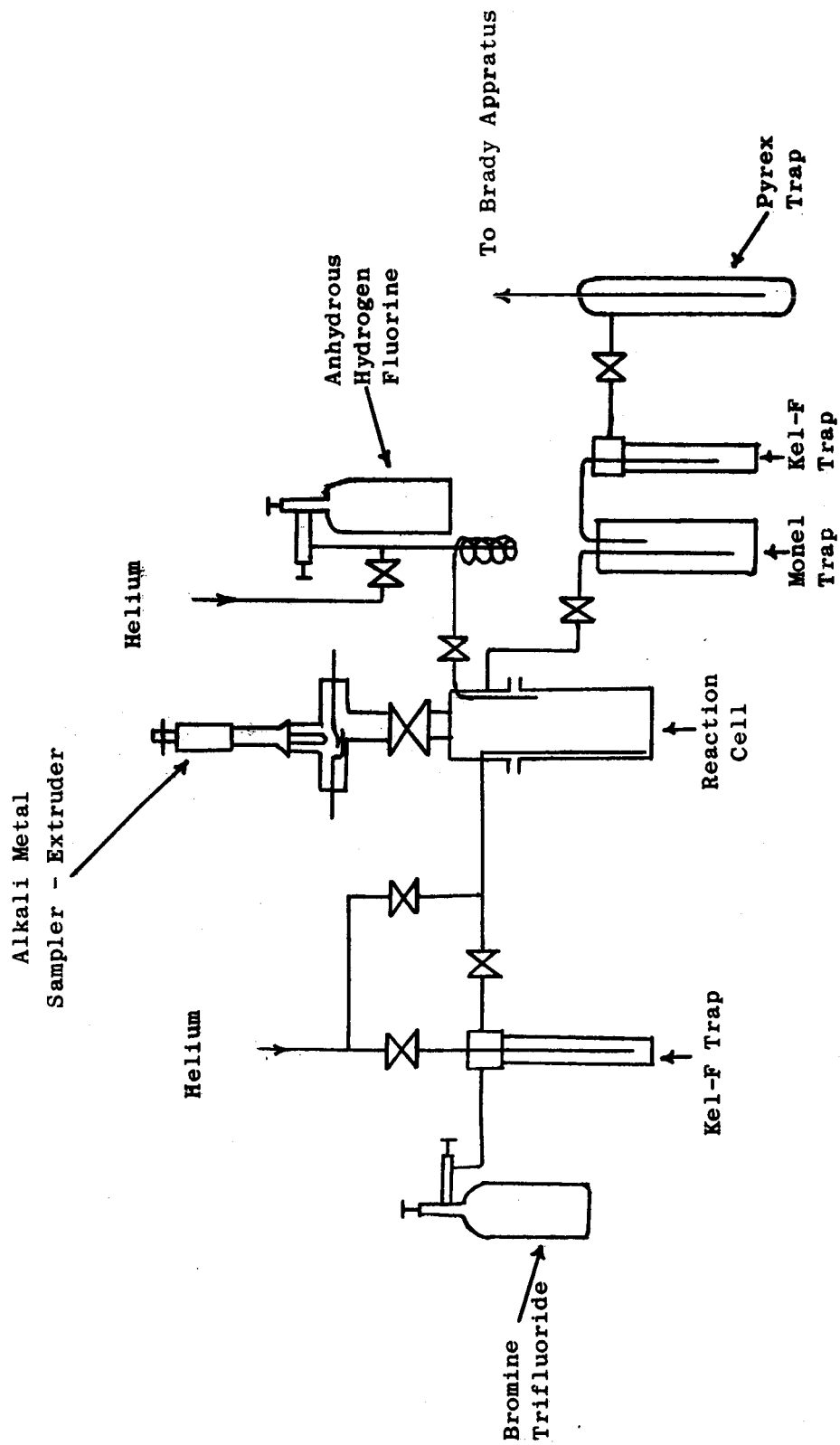


FIGURE I SCHEMATIC OF AHF - BrF₃ SYSTEM

With the cessation of work on the AHF-BrF_3 combination, the remaining effort was directed to a system involving BrF_3 alone. The successes obtained with this approach are covered in all the sections which follow.

APPARATUS

Figure 2 outlines the apparatus used for all the subsequent work with bromine trifluoride alone.

After alternate helium purging and evacuation, a known volume of BrF_3 may be distilled from the cylinder into Kel-F Trap A. Then by similar treatment, the reagent is transferrable to the Reaction Cell B. By means of a Teflon "O" ring the Alkali Metal Sampler-Extruder is bolted to the Cell. A Jamesbury Vacuum Ball Valve 8, with a 3/4" opening, provides for the introduction of samples. Means for purging the Cell with helium are provided through Valves 7 or 14. The helium originates from the NaK bubbler and through Valve 5 into 7. Alternately, the Cell may be evacuated through Valve 7 and 4 and through Trap J to the vacuum manifold, when 13 and 14 are closed.

The purpose of Trap H is to condense the volatiles originating from Kel-F Trap A. Preliminary pumping on BrF_3 in this trap through Valves 11 and 1 removes the bulk of the "impurities" before the bromine trifluoride is transferred to Cell B.

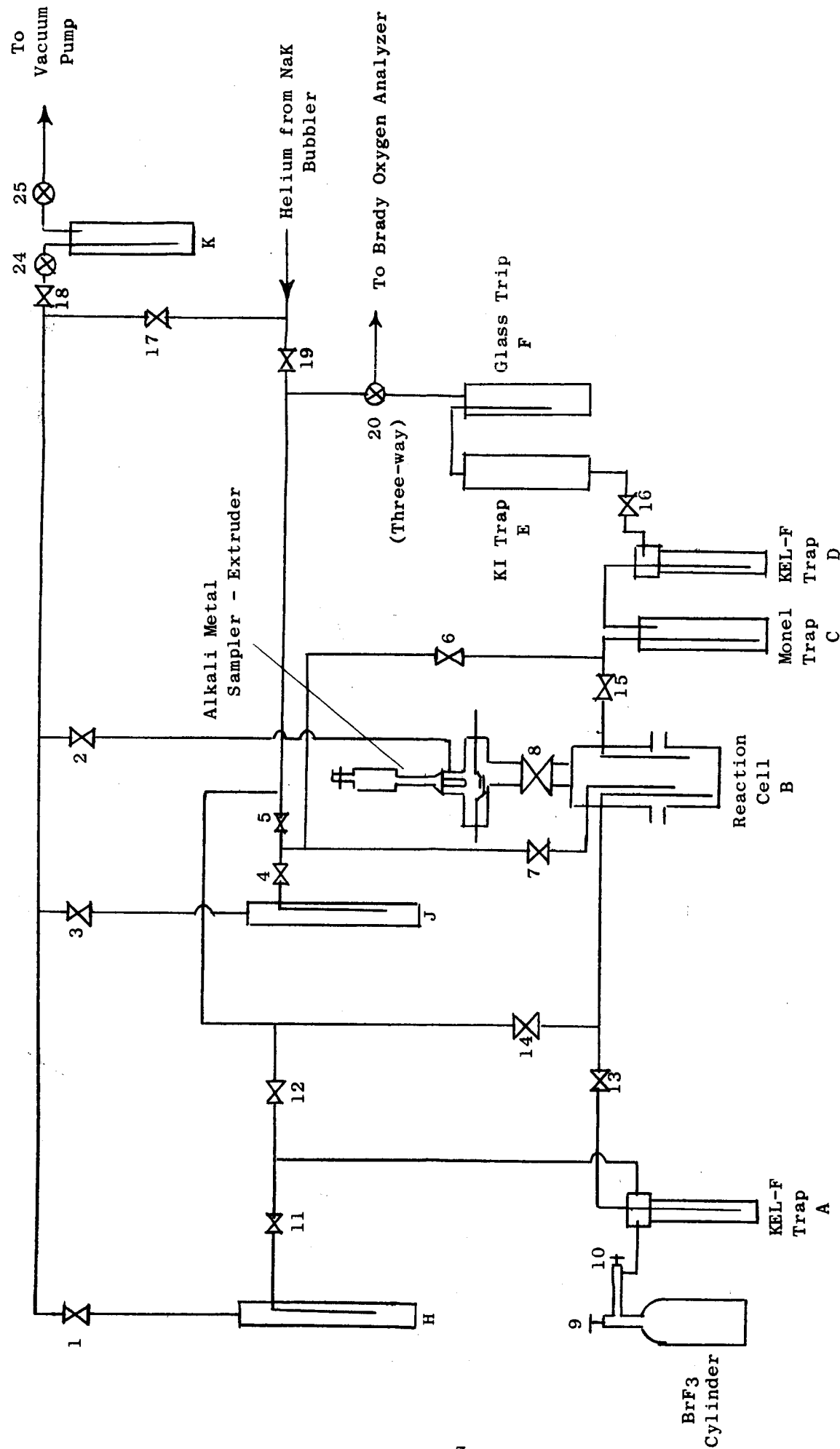


FIGURE 2 SCHEMATIC OF BrF_3 SYSTEM

When running a blank or a test sample in Cell B, the volatile end-products from the reaction with the BrF_3 are swept by the helium through Valves 5 and 7 with Valves 4, 6, 13, and 14 closed and to the aft-system through Valve 15. The aft-system consists of a Monel cold Trap C, Kel-F Trap D, KI Trap E, and liquid N_2 glass Trap F. Bromine and any fluorine are condensed in the system prior to the KI Trap E. This latter is a further precaution for the conversion of any Br_2 or F_2 to KBr and KF with the liberation of I_2 . The Iodine is easily condensed in the glass Trap F with liquid nitrogen.

When a sample is first introduced into Cell B, Valves 7, 13, 14, and 15 are usually closed. During this time, helium is allowed to pass through the aft-system through the by-pass Valve 6.

Only helium and liberated molecular oxygen (assuming no-leaks in the apparatus) sweep by the glass-trap F through three-way Valve 20 to the Brady Oxygen Analyzer where the oxygen may then be measured. The helium flow-rate is held at 125 ml/min. To determine the null point on the B & L Spectrophotometer attached to the Brady Analyzer, oxygen-free helium from the NaK enters through Valve 19 and the three-way Valve 20.

The Alkali-Metal Sampler-Extruder may be evacuated through Valve 2. A means for evacuating the helium lines is provided through Valve 17. The whole vacuum manifold may be isolated by means of Valve 18. Preceding the vacuum pump is a glass cold trap, isolated by Stopcocks 24 and 25. With a Dewar of liquid N_2 the halogens condense in the trap and, therefore, do not foul the pump.

All valves in the system are made of monel and are either of the bellows or diaphragm type. All connecting lines are monel or copper tubing. In this first construction, a large number of monel or brass swagelok fittings were used for the assembly.

DISSOLUTION OF POTASSIUM

It was demonstrated that the reaction of potassium with bromine trifluoride could be easily managed as a manipulative step without difficulty or violence.

The volume of the present Reaction Cell B, was limited such that additions over 0.5 g of K were not tried. As a generalization, 1.0 g of potassium reacts with 1.17 g of BrF_3 . However, to insure complete liberation of oxygen, the KF formed should be allowed to completely dissolve in the excess BrF_3 . The Kel-F Trap A held approximately 3.5 g of BrF_3 per cm length of tubing. For the tests, the Kel-F tubing A was usually filled to a height of 5-6 cm with BrF_3 before its transfer to Reaction Cell B. Therefore, no more than 21 g of BrF_3 were generally used.

On three different occasions, 0.5 g of potassium were added by means of the Alkali Metal Sampler-Extruder to the Cell B. A small copper crucible was held below the extruder. The potassium was cut and dropped into it while the Jamesbury Valve 8 was still closed. Then the crucible and its contents were admitted to Cell B through Valve 8.

The procedure used was identical for all tests with potassium or potassium bromate spikes (noted later) and would simulate one technique for the final analytical method:

- a. Reaction Cell B containing the BrF_3 was cooled in liquid N_2 to about -30°C and evacuated through Valve 7.
- b. The Alkali Metal Sampler-Extruder was evacuated through Valve 2. With the present system 2-3 microns were obtained.
- c. With valves 7, 13, 14, and 15 closed, the potassium was extruded, cut, and admitted to the Cell B, through the Jamesbury Valve 8.
- d. During this time, helium was allowed to sweep through the aft system through the by-pass Valve 6.
- e. The liquid N_2 Dewar was removed from the Cell B which, with its contents then was warmed up to $21-23^\circ\text{C}$ or room temperature. The elapsed time was usually 45-60 minutes because of the conductivity of the monel cell.

For an actual analytical determination, the subsequent procedure would consist of first closing Valve 6, then admitting helium through Valve 7, to sweep out the gaseous products and out through Valve 15 towards the measuring system.

In each of the three trials, the rise in temperature from -30°C to $+23^{\circ}\text{C}$ was measured on a Palmer thermometer with the thermocouple end attached to the leg on the Reaction Cell. No abnormal rise was noted. Evidently reaction occurs while the BrF_3 is melting at 9°C , the heat of reaction being overcome somewhat by both the heat of fusion of BrF_3 and the heat of solution of KF in it. The last of the three tests is covered later.

MEASUREMENT OF OXYGEN LIBERATED

The method for measuring oxygen alluded to in previous Quarterly Reports involves principles and apparatus established by Brady⁽⁷⁾ and improved upon by Silverman and Bradshaw⁽⁸⁾. In essence, oxygen is absorbed into an alkaline solution of sodium anthraquinone beta sulfonate, which changes the solution from red to colorless. The dynamic course of the oxidation is followed by noting the change in transmission on a spectrophotometer. When an oxygen-free carrier gas like helium is used at a constant flow-rate, as little as 0.005 ppm of oxygen may be detected. By a judicious design of the glass apparatus through which both the gas and solution pump and circulate, detection between 1 to 200 ppm is easily obtained. The accuracy depends somewhat on the choice of spectrophotometer, the quality of the carrier gas, and the ability to read the instrument and its optical response. Hydrogen, carbon dioxide, and nitrogen have no effect on the color of the solution.

A Bausch and Lomb #20 Spectrophotometer was used with a wave-length setting of 530 millimicrons. Because of the difficulty in scale reading, the instrument

was nulled at 20% T. The system shown in Figure 3 is originally calibrated by oxygen generated from an electrolytic cell containing dilute sulfuric acid solution. Figure 4 shows the curves obtained by applying the Faraday principle where the amount of oxygen liberated (in micrograms) is correlated with the percent transmission from the Brady apparatus. By a system of stopcocks, the reagent solution may be regenerated (i.e., reduced) by passing through an amalgamated zinc column on the apparatus. In this manner either 0% or 20% T may be obtained between runs. By means of the three-way stopcock (Figure 2, 20), helium may be admitted directly from the NaK bubbler to the Brady apparatus. Alternately, the helium from the NaK bubbler can pass through the entire system in Figure 2 and then be admitted to the Brady for oxygen read-out.

The efficiency of the NaK bubbler for removing oxygen is easily shown. With a flow-rate of 125 ml/min. the helium directly from the NaK bubbler showed no detectable change in % T on the B & L Spectrophotometer in the course of one hour.

Prior to any run, it was always deemed advisable to check out the Brady apparatus and the Spectrophotometer by running helium through it for some time. A continuing zero % T reading was indicative of "good" helium and a responsive instrument.

To check the tightness of the present system (which leaves something to be desired), the helium was passed first through its entirety and then through the aft-system. The results on the total system are covered later. A typical run on the aft-system, that is to say, by-passing the Reactor Cell B and

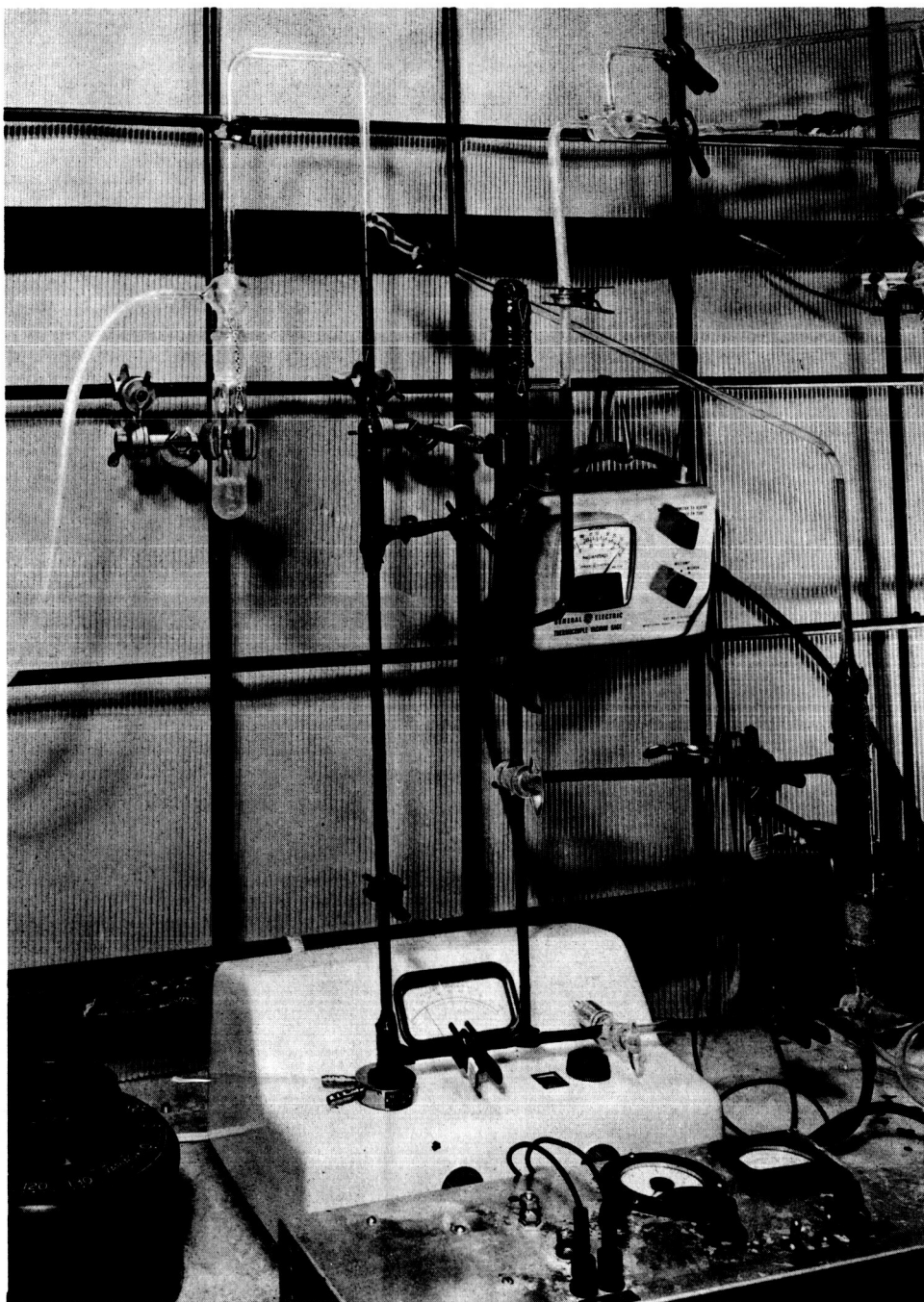
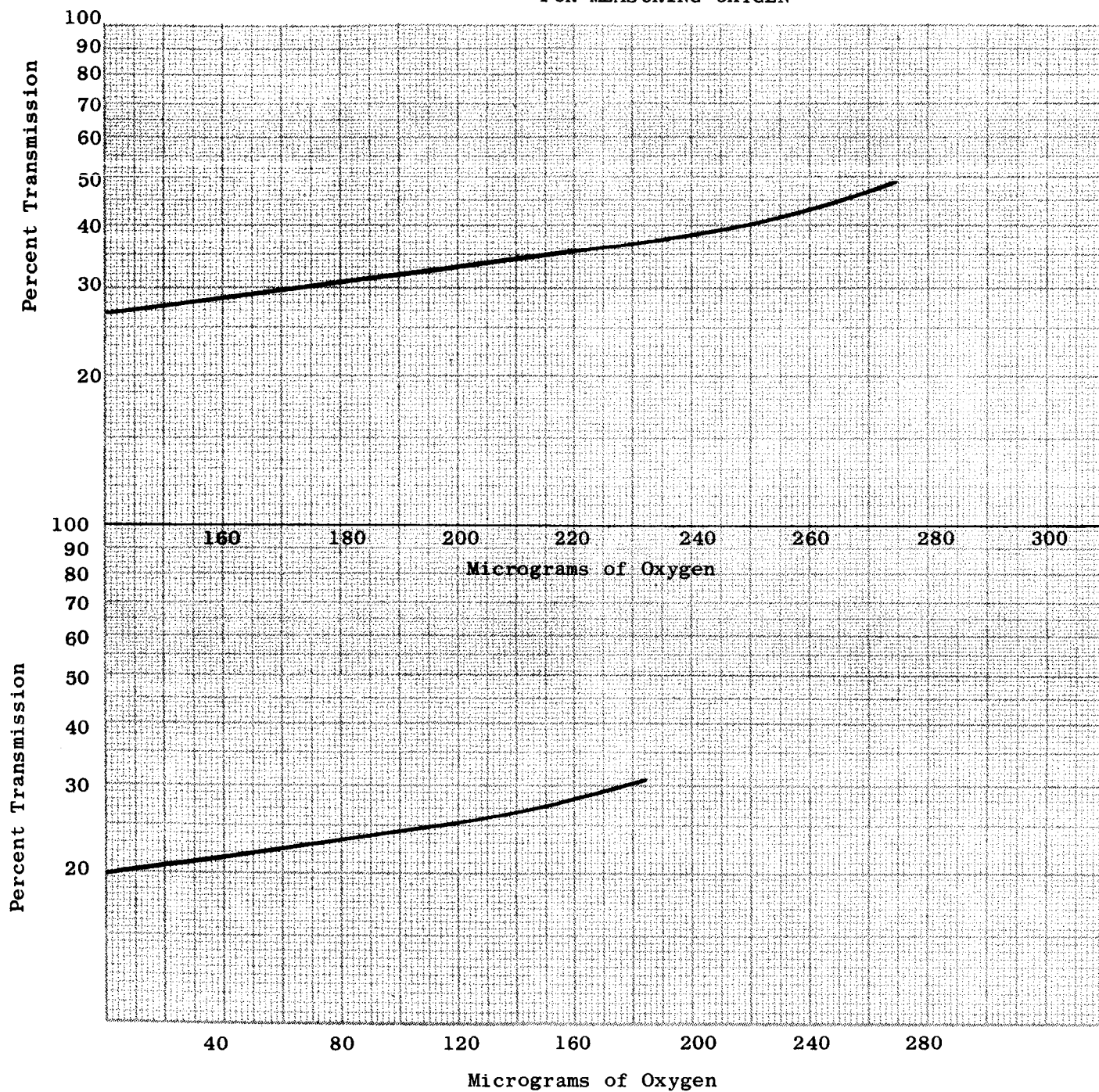


Figure 3. Brady Apparatus for Oxygen Determination (C2062218)

FIGURE 4 CALIBRATION CURVE - STANDARDIZATION OF BRADY APPARATUS
FOR MEASURING OXYGEN



entraining the helium through Valve 6 gave a "leak rate" equivalent to five micrograms of oxygen in one hour. The actual % T increased from 20.0 to 20.2 in two hours is equivalent to 10 micrograms of O₂. This value, instead of 0.0 micrograms indicated some small leaks in the system.

It is important to note at this point that the absence of oxygen in BrF₃ was confirmed in the above manner. Some BrF₃ was condensed in Kel-F Trap A and then frozen with a Dewar of liquid nitrogen. The fluorothene tube was then disconnected from the monel nut and interchanged on the nut of Kel-F Trap D (see Figure 2). Then, while the BrF₃ was still frozen, helium was admitted through Valve 6 to sweep out any oxygen/air added extrinsically above the frozen bromine trifluoride. The sodium anthraquinone beta sulfonate solution in the Brady was then purposely reduced back to 20% T. The passage of helium over the BrF₃ was then continued while the interhalogen warmed up to room temperature. After an additional hour, the "leak rate" registered on the spectrophotometer was the same five micrograms of O₂/hour rate. The above is a demonstration that BrF₃ may be obtained oxygen-free and maintained as such in a closed system for analytical purposes.

Tests were then made to ascertain the "leak rate" of the whole system. This included the Reaction Cell B, the Alkali Metal Sampler-Extruder, the bolting and gasketing joining them together, and the Jamesbury Valve 8. It was anticipated, in advance, that because of the excessive number of fittings and valves, a noticeable leak rate would be obtained.

With 20-30 ml of BrF_3 in the Reaction Cell B and helium passing at the rate of 125 ml/min., three successive runs on three separate days gave excellent agreement. The results are shown in Table I. The leak rates obtained were 99, 99, and 106 micrograms of oxygen per two hours! These indicate that if an actual chemical analysis of oxygen in potassium could be concluded within an hour, the maximum blank would be only 50 micrograms of oxygen with the present apparatus. Later on, it will be noted that other leak rates were obtained. These were the result of a series of breakdowns with the apparatus used.

RECOVERIES FROM OXYGEN-BEARING COMPOUNDS

It was noted by Emeleus⁽¹⁾ that oxygen was liberated quantitatively from iodates and bromates. As was the case with oxides, macro-sized samples had been used to conclude that the BF_3 did, indeed, react completely with these oxy-acid salts. It is to be noted at this point that with carbonates only one of the three oxygen atoms is liberated as molecular oxygen. This is interesting since it suggests that K_2CO_3 in potassium would not interfere with the oxygen determination by giving a false reading of total oxygen.

Towards the development of a reliable method for oxygen in alkali metals here, it was necessary to demonstrate conclusively that the bromate reactions, for example, would take place quantitatively with micro quantities of oxygen three to five orders of magnitude less than previously recorded.

TABLE I

OXYGEN LEAK RATE THROUGH ENTIRE BrF_3 SYSTEM

Time (Min.)	Trial 1 8-8-63 % T	Trial 2 8-12-63 % T	Trial 3 8-13-63 % T
0	20.0	20.0	20.0
5	20.0	20.4	20.0
10	20.1	20.9	20.1
15	20.3	21.0	20.3
20	20.7	21.3	20.5
25	21.0	21.4	20.7
30	21.1	21.6	20.8
35	21.3	21.8	20.9
40	21.6	22.0	21.0
45	21.9	22.1	21.2
50	22.1	22.2	21.3
55	22.3	22.3	21.4
60	22.6	22.4	21.7
65	22.9	22.6	21.9
70	23.0	22.9	22.0
75	23.2	23.0	22.2
80	23.4	23.1	22.5
85	23.5	23.2	22.7
90	23.7	23.3	23.0
95	23.8	23.4	23.3
100	23.7	23.5	23.8
105	24.2	23.7	24.0
110	24.2	24.0	24.1
115	24.2	24.1	24.3
120	24.3	24.3	24.6
Leak Rate $\mu\text{g O}_2/2 \text{ Hrs}$	99	99	106

To test the above, a series of "spikes" were prepared as follows. Small, copper foil shallow dishes were made approximately 0.5" D at the top and 0.25" high. A microburet syringe was used to dispense a solution of potassium bromate, KBrO_3 , containing 750 mg O_2 /ml to the copper dishes. This syringe was calibrated at 0.500 microliters per division, where one division equals 0.001" of travel. Sufficient KBrO_3 solution was added to give dishes containing 25, 100, and 150 micrograms of oxygen. Since the bromate is stable, the small amount of liquid was easily removed by evaporation at 100 - 110°C in an oven. The dishes, now containing the dried KBrO_3 were stored in a desiccator until ready for use.

For any one run, a copper dish and its contents was carefully placed by platinum-tipped tweezers just above the Jamesbury ball Valve 8. The Upper Alkali-Metal Sampler-Extruder system was then evacuated. For the run, the same procedure for obtaining the "leak rate" was used. While helium was purging the by-pass system through Valve 6, the BrF_3 in the Reaction Cell B was frozen to about -25°C. With the Cell B isolated, Valves 7, 13, 14, and 15 being closed, the Jamesbury Valve 8 was turned momentarily to admit the copper dish and the adhering KBrO_3 . The cell was then allowed to warm up to room temperature (ca, 22°C) over the course of 45-60 minutes. During this time, as eventually proven, the reaction between the KBrO_3 and the BrF_3 is complete. Emeleus' reported studies were 75°C.

Valve 6 was then closed and Valves 7 and 15 opened. Simultaneously, the Brady apparatus was nulled on 20%T and set on ANALYZE position. The gaseous

products above the BrF_3 liquid were swept with the helium (125 ml/min) by diffusion through the aft-system of traps, etc., and thence the oxygen and carrier gas passed through the Brady apparatus. Just prior to each run, the leak rate was obtained in exactly the same manner without the addition of the KBrO_3 and copper dish. The transmission curves were plotted on semi-log paper, and the differences calculated to weight of oxygen from Figure 4. While the present methods of measurement require refinement, the following results in Table II may be noted. At room temperature successful recoveries were obtained on all samples. A copper dish introduced without KBrO_3 additive showed no oxygen recovery. The ability of the system and the choice of reactions to measure oxygen specifically and quantitatively by the interaction of micro quantities of an oxygen-bearing compound with an excess of bromine trifluoride has been demonstrated.

TABLE II

RECOVERY OF OXYGEN FROM THE REACTIONS OF KBrO_3 AND BrF_3

<u>Micrograms of Oxygen Added as KBrO_3</u>	<u>Micrograms of Oxygen Recovered</u>
150	132.4
150	152
100	94
25	27

The data connected with the four successful runs is given in Tables III and IV as well as Figures 5, 6, 7, and 8.

TABLE III

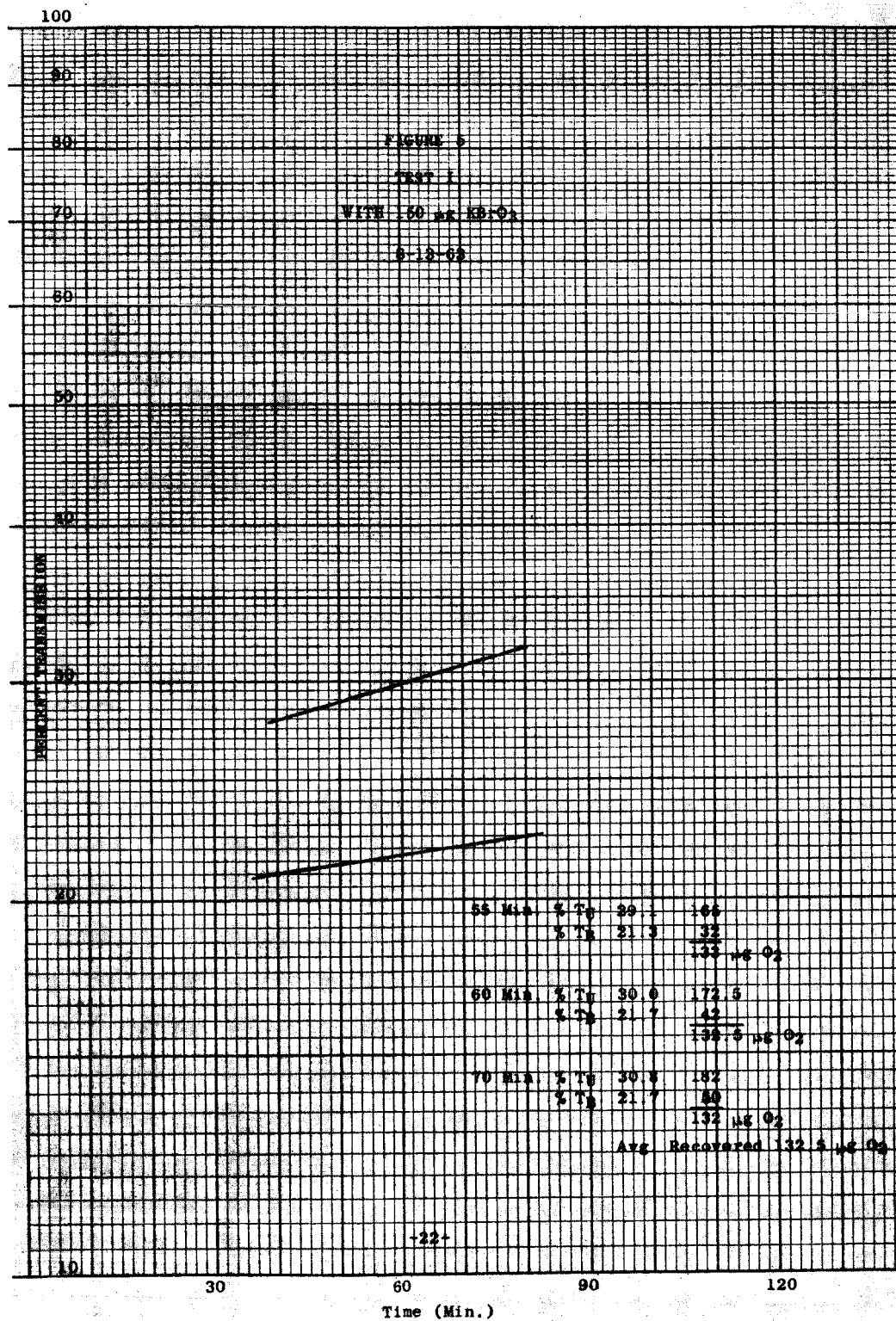
TESTS ON RECOVERY OF OXYGEN FROM KBrO_3 ADDITIONS TO BrF_3 Test I
(See Figure 5)
150 μg O_2 Test II
(See Figure 6)
150 μg O_2

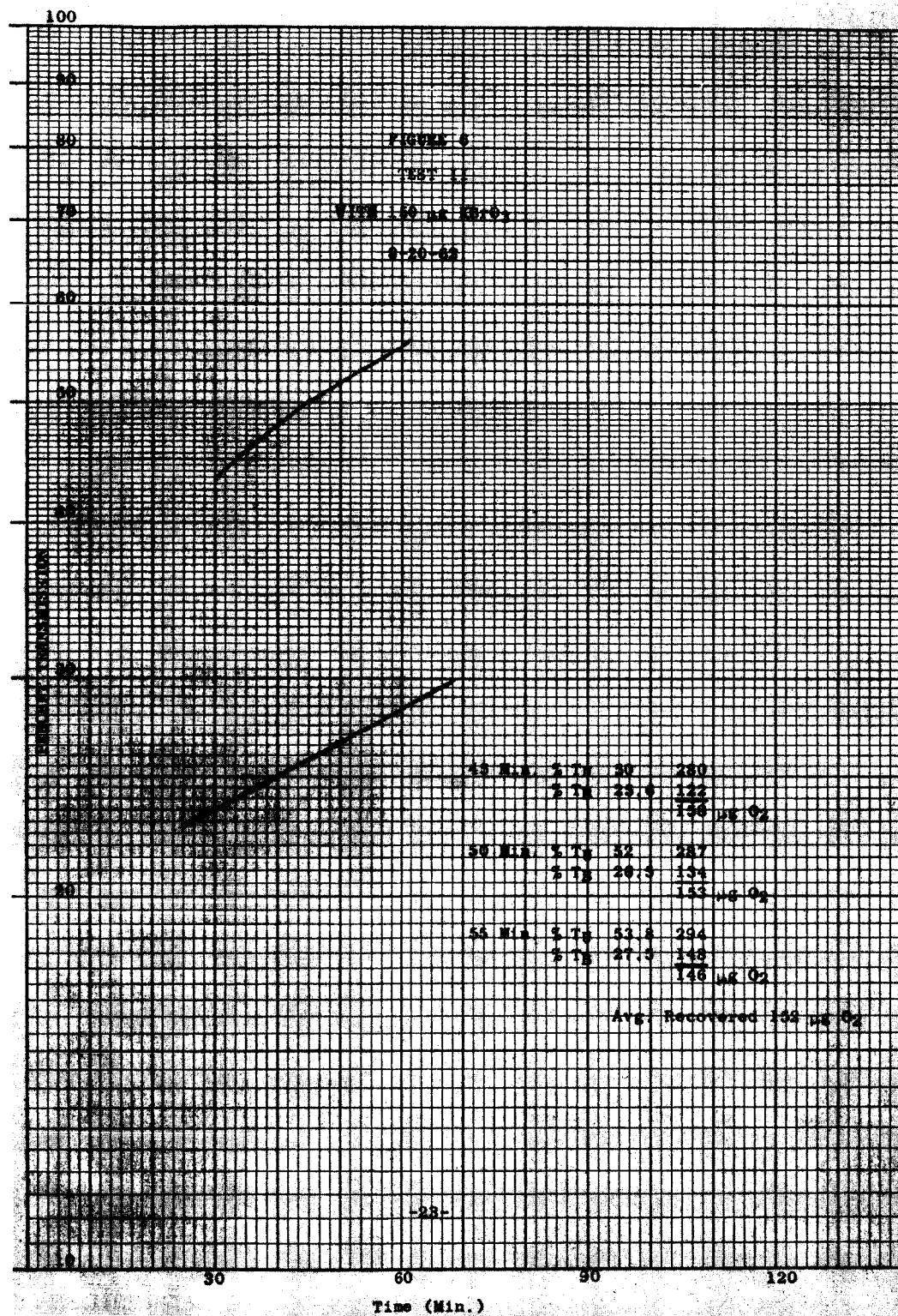
<u>t(min.)</u>	<u>% TB</u>	<u>% TU</u>	<u>t(min.)</u>	<u>% TB</u>	<u>% TU</u>
0	20.0	20.0	0	20.0	20.0
5	20.0	20.9	5	20.0	20.0
10	20.1	22.0	10	20.8	21.2
15	20.3	23.0	15	21.6	29.3
20	20.5	24.3	20	22.1	36.3
25	20.7	25.9	25	22.9	40.5
30	20.8	27.3	30	23.3	43.4
35	20.9	27.8	35	24.1	45.5
40	21.0	28.2	40	25.0	47.8
50	21.2	29.1	50	26.5	52.0
55	21.3	29.7	55	27.5	53.8
60	21.7	30.0	60	28.4	55.6
65	21.9	30.3			
70	22.0	30.8			
75	22.2	31.3			
80	22.5	32.0			

TABLE IV

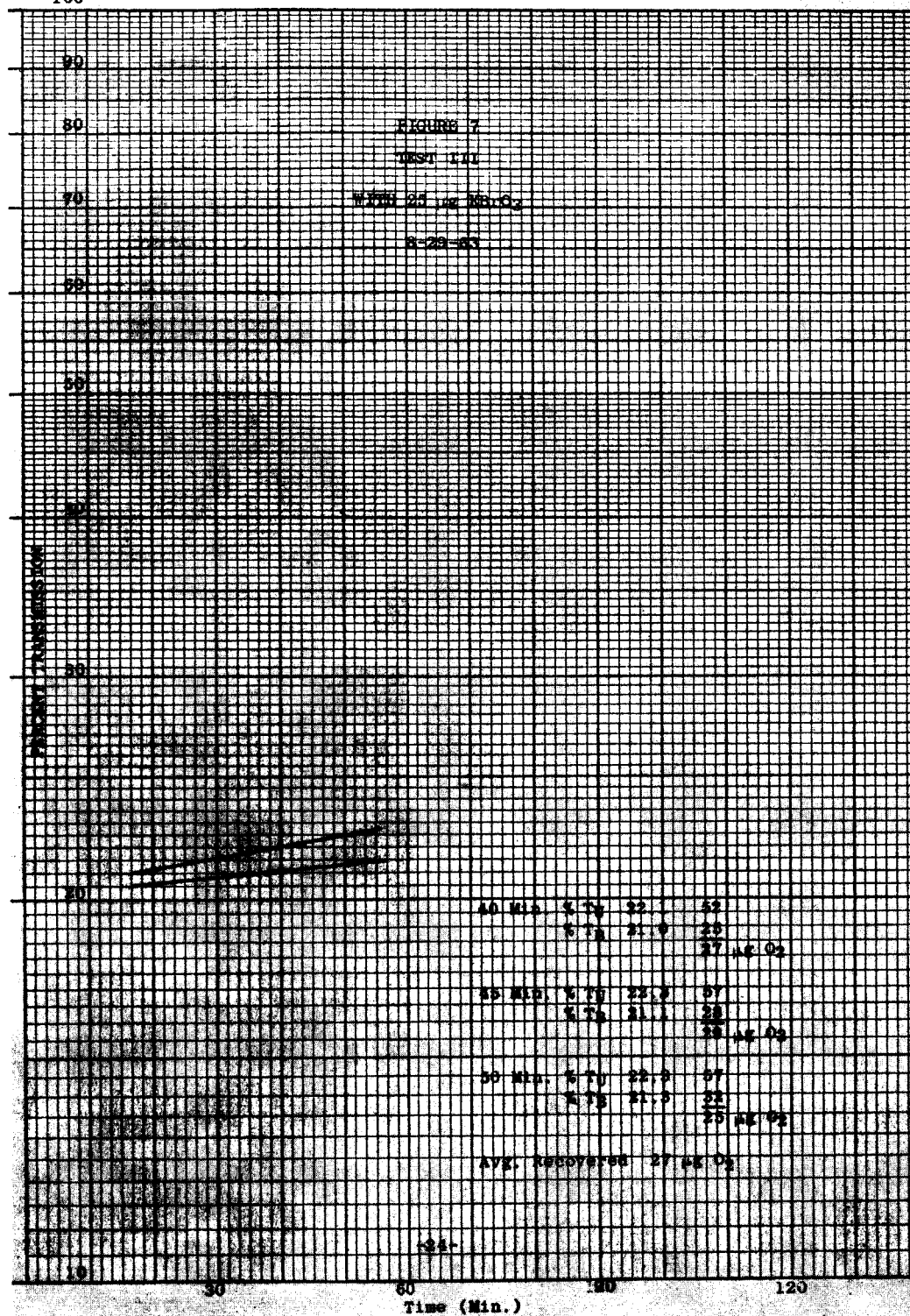
TESTS ON RECOVERY OF OXYGEN FROM KBrO_3 ADDITIONS TO BrF_3

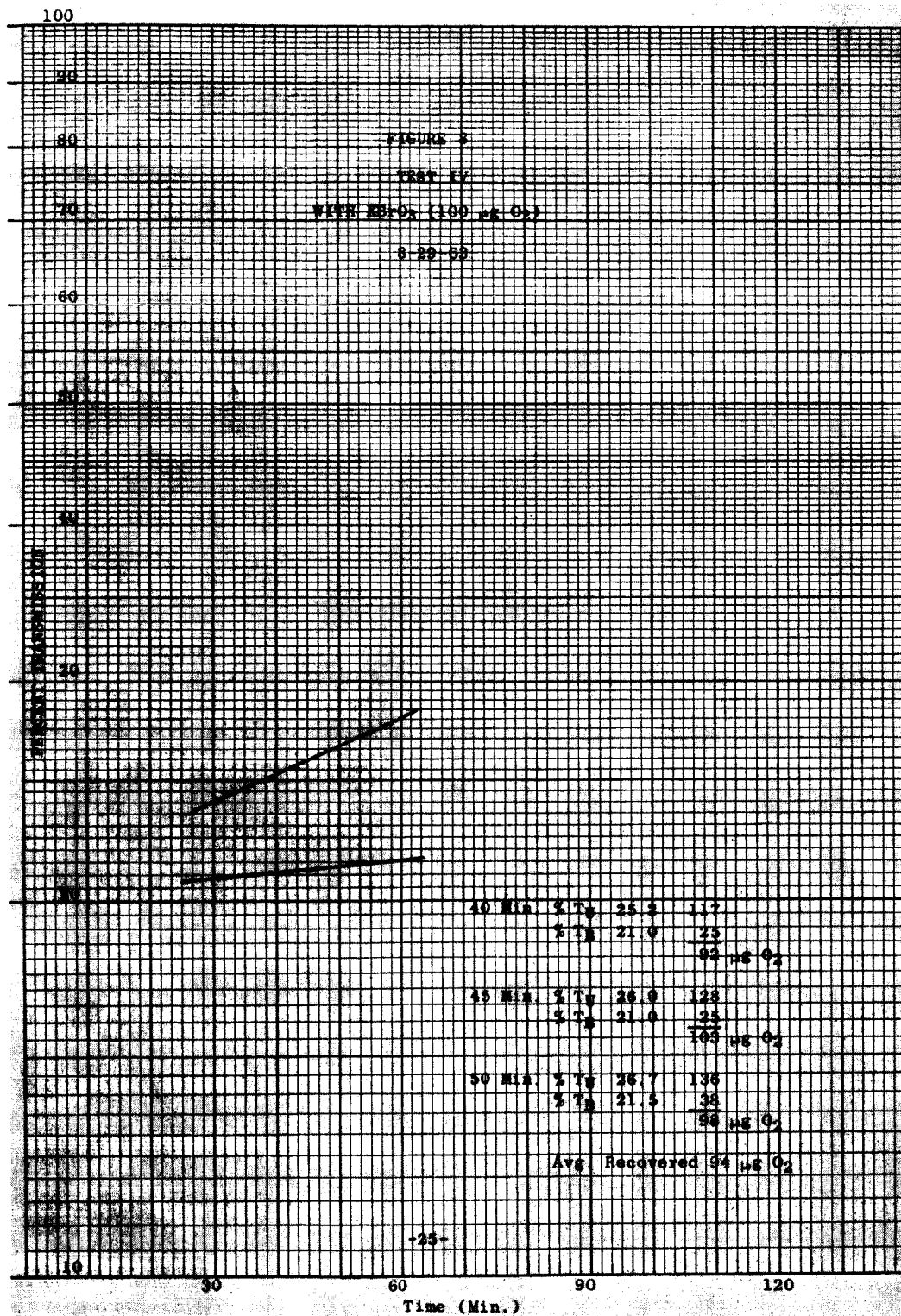
Test III (See Figure 7) 25 μg O_2			Test IV (See Figure 8) 100 μg O_2		
<u>t(min.)</u>	<u>% T_B</u>	<u>% T_U</u>	<u>t(min.)</u>	<u>% T_B</u>	<u>% T_U</u>
0	20.0	20.0	0	20.0	20.0
5	20.0	20.0	5	20.0	20.0
10	20.1	20.0	10	20.1	20.4
15	20.2	20.7	15	20.2	21.3
20	20.5	21.0	20	20.5	22.2
25	20.7	21.3	25	20.7	23.0
30	20.9	21.7	30	20.9	24.0
35	21.0	21.9	35	21.0	24.7
40	21.0	22.1	40	21.0	25.2
45	21.1	22.3	45	21.1	26.0
50	21.3	22.4			





100





RECOVERY OF OXYGEN FROM POTASSIUM

One of the three tests mentioned previously for interacting potassium and bromine trifluoride was actually carried out after the KBrO_3 experiments were completed. In the short time remaining, and with a known deficiency with the present Alkali-Metal Sampler-Extruder, it was decided to add a contaminated potassium sample to the BrF_3 in the system under conditions exactly similar to those used for the bromate additions. With the systems blanked as usual, any oxygen finally measured on the Brady apparatus had to be derived from that contained within the 0.5 g of potassium added. About 500 micrograms of oxygen resulted. It was successfully demonstrated, therefore, that the oxide(s) within the potassium had reacted with the BrF_3 as evidenced by a large recovery of oxygen on the Brady measuring system.

DISCUSSION AND CONCLUSIONS

These feasibility studies indicate that a new analytical method involving the use of bromine trifluoride can be developed for the specific determination of oxygen, at levels of 5 to 100 ppm in alkali metals.

It is necessary to refine the present apparatus using the established principles previously developed. The requirement of a low blank relative to the amount of oxygen to be determined increases the necessity for a more leak-tight system. The objective is to reduce the blank or "leak" rate to acceptable levels of less than 10 micrograms of oxygen per hour. Any

redesign would eliminate, as much as possible, all types of fittings. Their replacement with brazed or welded construction between the various lines of communication is advantageous. Only aluminum, copper, monel, and nickel should be used since they are inert to bromine trifluoride. Teflon or other fluocarbons may be used in those sections deemed necessary, particularly where sealing and gasketing are required. All valves and traps must pass the rigid requirement of maintaining high vacuum and corrosion resistance.

Emphasis is needed on that portion of the system for the transfer, purification and storage of BrF_3 for the intermittent addition of this reagent to the main reaction cell. The main reaction cell and section could be completely redesigned and enlarged to accomodate larger volumes of bromine trifluoride. This would allow for the sequential determination of a number of samples of alkali metal without the necessity for disassembly of the cell between runs. When an excess of BrF_3 is present, the addition of any one sample of potassium, for example, would not expend the reagent or restrict its use from further sample additions.

The success of procedures with alkali metals depends largely on the method of sampling. To this end a more refined vacuum extrusion-sampler system is required. A high vacuum system employed with it requires modification and would have to connect with the entire reaction system differently.

Refinements are required to maximize the utility of the present design of apparatus incorporating the Brady principle. These include certain changes

in stopcocks and improving the over-all rigidity. Further, the use of a precision grade 1 cm square quartz absorption cell for the Spectrophotometric readings is suggested. Preferably, a high precision narrow-band recording spectrophotometer capable of charting transmission changes versus time at a fixed wave-length should be used in conjunction with the Brady apparatus. Another feature necessary for accuracy in the range of oxygen values to be measured is the ability to superimpose both the blank and sample runs on the same chart. Linear scales may be used by the simple expedient of measuring absorbancy instead of the logarithmic percent transmission. To increase the sensitivity further, a selector switch for altering the scale should be an integral part of the instrumentation. Change-over from 0-100% T full scale to 0-10% T full scale would be ideal for the measurements contemplated.

Of importance is the procurement of good sample grades of potassium or other alkali metals. In this respect, close liaison is necessary with sources for obtaining suitable potassium for the test runs. The levels of oxygen found by others must be factored into the work. However, the specificity offered by a successful BrF_3 method may yield results that differ from those reported by other procedures wherein the present state-of-the-art recognizes that the apparent oxygen values are the summation of a number of interfering impurities.

Further work on the controlled addition of varying amounts of potassium, with and without purposeful additions of potassium bromate, is needed to test recoveries. It was demonstrated that the bromate (KBrO_3) releases all of its oxygen quantitatively and that the compound can be easily introduced

into the system along with potassium. This presents an advantage heretofore rather impossible to ascertain. Statistical data may be obtained easily as a result of this proposed approach. Other impurity compounds found in potassium such as K_2CO_3 could be similarly introduced.

To finalize and establish the BrF_3 method for general spread use, a number of tests must be made. Statistical methods should be used to properly interpret all the data obtained:

- 1) A series of analyses with a number of uniformly pure potassium samples to establish the precision.
- 2) A series of analyses with potassium and the addition of known amounts of potassium bromate to establish the useful range of the method.
- 3) A series of analyses to establish the sensitivity of the method, particularly at the 5 micrograms of oxygen range.
- 4) A series of analyses to establish the number of individual determinations that can be made on the same batch of bromine trifluoride without interruption or disassembly of the main reaction cell from the apparatus.
- 5) A series of analyses with varying sample sizes or weights or potassium to determine the bias on accuracy or the presence of constant errors.
- 6) A series of analyses with sodium metal to determine the initial applicability to other alkali metals.

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